

## FEATURES OF THE FORMATION OF THE OXIDE LAYER DURING THE ANODE VIBRATION

KOLENCHIN N. F

*Professor, Chief Researcher, Center for Advanced Research and Innovation Industrial University of Tyumen, Russia*

### ABSTRACT

*The vibration effect of the ozonated liquid in the interelectrode gap on the oxide layer growth has been established. The formation stages of the strengthening coating are determined in accordance with the dynamics of changes in the current strength and anode oscillation frequency. The ultrathin surface layer is investigated.*

**KEYWORDS:** Anodizing, Ozone, Vibration, Cavitation, Spectra, Phase Composition & Microstructure

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### INTRODUCTION

Anodizing process activation of aluminum alloys by ozonating an aqueous solution of sulfuric acid [1] offers a number of advantages in the formation of wear-resistant coatings. The insignificant appearance of ozone in the working solution is noted by a number of authors [2, 3], as the result of electrochemical processes. Artificial, controlled injection into the interelectrode gap of a component with exceptional oxidizing properties and latent heat of decomposition [4] changes the mechanism of the reactions taking place inside the pore space with the corresponding structural and phase changes during oxidation. Considering that the ozone participation effectiveness is determined only by its fraction dissolved in the electrolyte, it becomes necessary to find ways to increase the liquid–gas solubility.

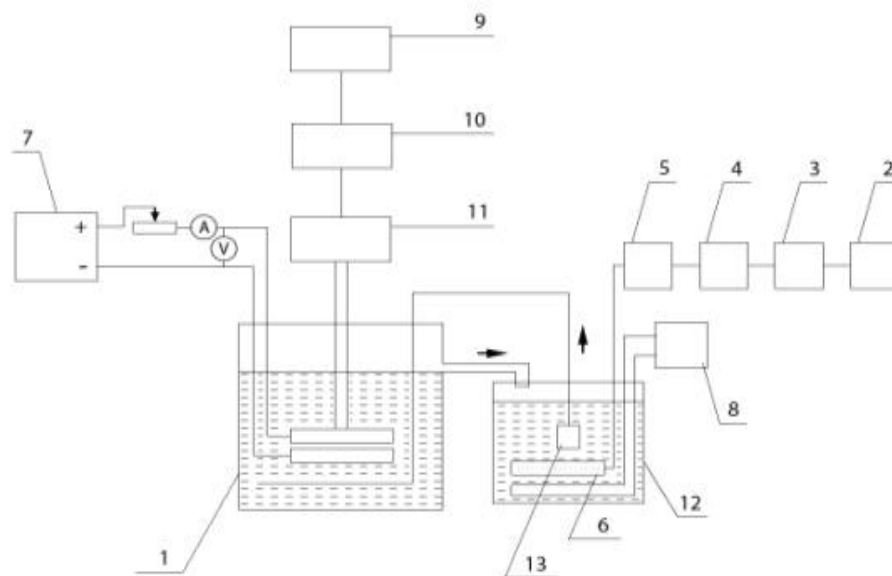
There is a method of acoustic exposure with cavitation manifestations [5], as a result of which gas bubbles break into smaller fractions with the formation of high pressures in the microvolume and a temperature jump at the moment of the cavitation case [6]. Similar phenomena are manifested during objects' vibration in a number of strengthening technologies [7] as well as removal of metal associated processes [8]. The vibration of the cathode [9] is used in the electrochemical treatment of super hard materials. At the time of the instrument reversal, a hotbed of cavitation is formed with a hydrodynamic explosion and electrolyte boiling. The gas fragmentation bubbles with unreacted ozone by vibrating the fluid in the interelectrode gap forms the basis of the studies presented.

### EXPERIMENTAL PART

The air mixture was pumped by a compressor 2 into the ozone generator 4, previously passing through the dehumidifier 3. The flow rate of the ozone-air mixture was controlled by the rotameter 5 and through the bubbler 6, the flow entered the storage tank 12 with electrolyte. The ozonated solution was cooled by the thermal installation 8, which was pumped into the tank 13 by the pump 13. A selenium rectifier 7 was used as a current source. A low-frequency signal generator 9, a signal amplifier 10 and a vibration generator 11 were used to impart oscillations to the anode. The distance between the electrodes corresponded to the minimum possible. The maximum amplitude of oscillation was 2 mm. The cathode was fixed motionless. Samples of size 20 x 20 x 3 mm were made of AD31

alloy. The ozone concentration in the air was kept constant and corresponded to 3 mg/l. A 10% solution of sulfuric acid was used as an electrolyte. Studies were conducted in the mode of incident power.

Figure 1 shows a scheme of the experimental setup.



**Figure 1: Anodizing Scheme for Anode Vibration in the Ozonated Electrolytic Solution.**

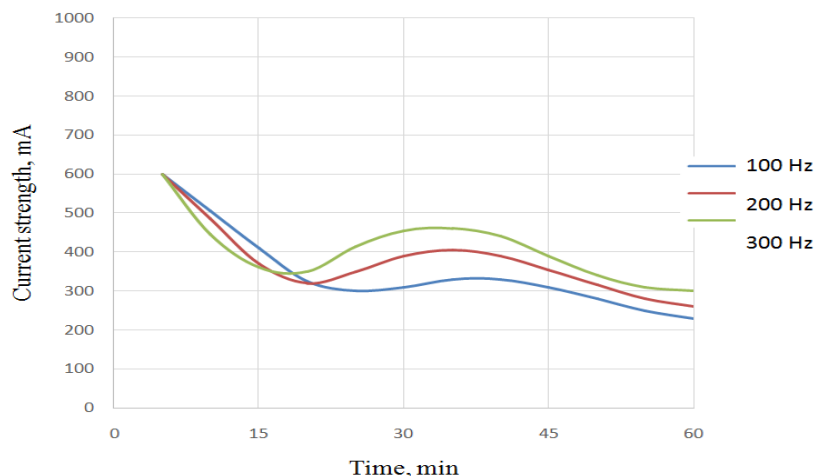
## RESULTS AND DISCUSSIONS

The collapse of a gas bubble has a definite direction towards a solid surface, with the release of a large amount of energy at the interface of the liquid and solid phases. Due to the size reduction of the gas bubble, the area of contact with the liquid and its dissolution in it increases [6].

The effect of anode vibration on the ozone dissolution process in the electrolyte was determined in two stages. At the initial stage, in a 10% sulfuric acid, electrolyte cooled to 10°C, two electrodes were placed parallel to each other at a distance slightly larger than the amplitude of oscillations. Consistently, for 15 minutes, at frequencies of 100 and 300 Hz, reciprocating movements of one of them was performed without connecting an electric current.

The degree of dissolution of ozone in the electrolyte was determined by an ozonometer. The concentration of dissolved ozone in the electrolyte with the anode vibration at a frequency of 100 Hz increased by 13%, and with the vibration at a frequency of 300 Hz by 24%. A further increase in the oscillation frequency to 400 Hz changed the ozone saturation rate by only 5%. Thus, the range of vibrations was determined from 100 to 300 Hz.

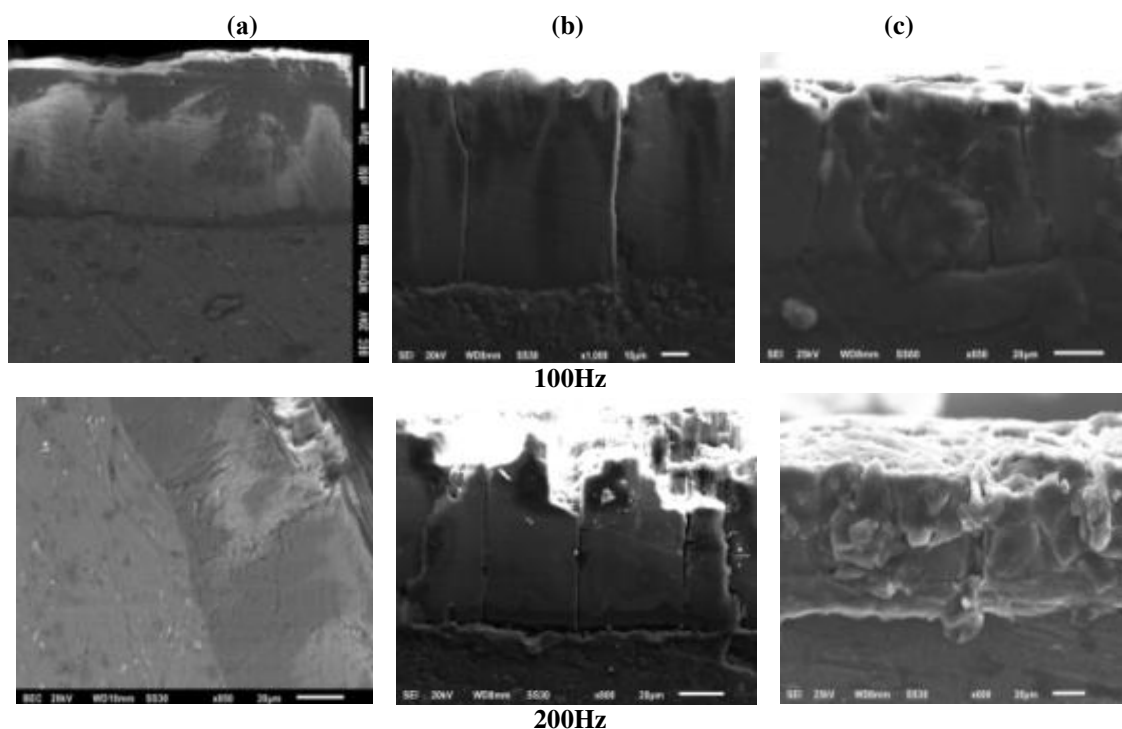
The second stage of research was carried out with the current source turned on. Visual observation of the reaction zone between the two electrodes showed intense gas formation in the frequency range of 100–300 Hz. The appearance of small bubbles created the effect of electrolyte boiling up. The dynamics of the current change at the initial 25 V forming voltage is shown in figure 2. At the initial stage of anodization, a decrease in the current is observed. After 15–20 minutes, the current is leveled with a further increase at the 25<sup>th</sup> minute.

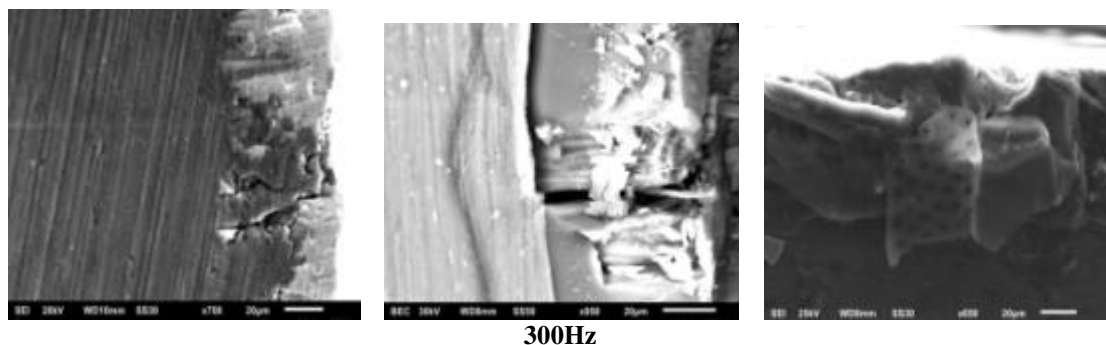


**Figure 2: Changes in the Forming Current during the Anode Vibration in the Ozonated Electrolyte.**

The dynamics of the changes occurring in the structure is shown in Figure 3. Microanalysis has determined that the oxide layer in the first 15 minutes for all anode oscillation frequencies is formed at high speed without visible deformations (Figure 3(a)). At the moment of current equalization, the stage of intensive cracking begins (Figure 3(b)) along filiiform pores. The appearance of cracks reduces the resistance of the coating, which is reflected in the diagram by the area of increasing current for the next 10 minutes. The moment of its decrease indicates the beginning of the encrustation of fracture sites and an increase in the resistance of the film. The nature of the surface is similar to the ridged texture.

With an increase in the frequency of vibrations, the texture is clearly pronounced. When the anode vibrates at a frequency of 300 Hz, a separate matrix fragment of the oxide film is clearly observed (Figure 3(c)), with a classical hexagonal shape, cut off from the base.





**Figure 3: Microstructure change during the Anode Vibration.**

A pore is a mini-vessel with a bottom. The oscillating anode gives fluid motion and stimulates the process of gas formation, creating pressure in the pore volume. The larger the channel diameter, the higher the gas tension. The maximum tension occurs at the time of passage of the return point of the anode from the cathode. The culmination is associated with a drop in pressure and the occurrence of cavitation, which can cause cracks and ruptures in the emerging pore.

X-ray photoelectron spectroscopy was used to study sample surfaces formed in a 10% sulfuric acid solution at an electrolyte temperature of 10°C, an oscillation frequency of 100 Hz (No. 564), 300 Hz (No. 575) and an initial forming voltage of 50 V.

Spectral analysis determined the elements' concentration on the surface layers of the samples in atomic percentages, and are shown in table 1. The concentrations were calculated from the integral intensities of the corresponding spectra, taking into account the coefficients of elemental sensitivity and the Specs Lab databases.

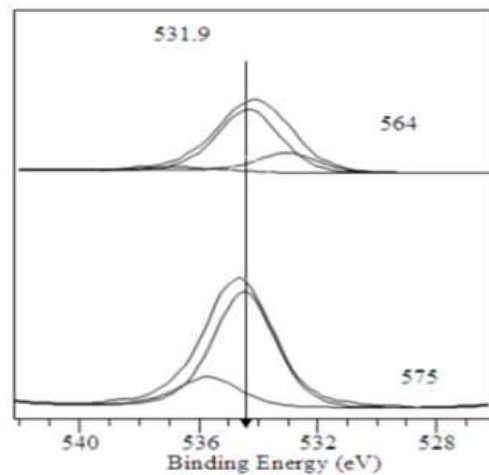
**Table 1: The Content of Elements in the Surface Layers of the Samples 5, 64, 575 and Reference Aluminum Sample at %.**

Sample	Depth, nm	O	Al	Si	S	C(o)/C(met)
564	0	32.1	7.4	1.4	tr.	3.41
	0,5	25.9	12.6	0.6	tr.	2.05
	5	24.9	16.0	tr.	tr.	1.55
575	0	37.6	12.8	2.4	tr.	2.48
	0.5	33.6	21.4	2.2	tr.	1.42
	5	33.9	24.7	2.2	tr.	1.26
Reference Al	0	33.1	19.9	0.0	0	1.67
	0.5	45.3	47.7	0.0	0	0.95
	6.5	7.9	87.6	0.0	0	0.09

The reference and samples' surface layer is carbon saturated, the content of which at a depth of 5 nm is not more than 4 at %. The rightmost column contains the ratio of the total oxygen concentration to the total aluminum and silicon concentration. From table 1, it is clear that the outer layer contains oxygen. The ratio of oxygen concentration at a depth of 0.5–5 nm to the aluminum concentration, which corresponds to 1.5 for the stoichiometry of  $\text{Al}_2\text{O}_3$ , shows that for sample No. 564, this is a much higher indicator. Sample No. 575 indicates the presence of silicon throughout the entire depth under study. XPS oxygen peaks are broadened and multi component, which is associated with both the heterogeneity of the charging surface and the oxygen presence in nonequivalent chemical states.

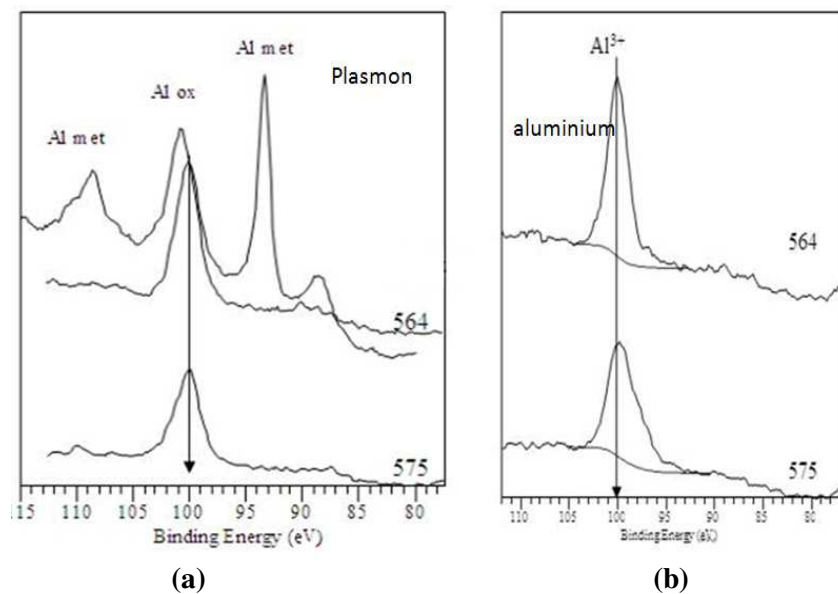
Figure 4 shows the experimental oxygen spectra without scale calibration. The arrows in the figure show the true

value of the binding energy of oxygen peaks (O-Al) before etching from the surface areas with maximum charging.



**Figure 4: Oxygen Spectra at a Depth of 5 nm without Scale Calibration for Charging the Surface.**

Figure 5 shows that the aluminum spectra of sample 575 are **one-component**. However, the spectra of the sample 564 surface have several peaks, but they all refer to oxidized aluminum ( $\text{Al}^{3+}$ ) since the spectrum of the Auger region of the line of metallic aluminum is not observed, and the Auger peak of the oxide is single. Thus, from the presented Figures 4 and 5, it follows that there is a non-uniform surface charging due to inhomogeneities in the composition of the surface layer. The main intense peak of oxygen is of oxygen bonded to aluminum ( $\text{Al}^{3+}$ ). This peak after scale calibration has a binding energy value of 531.9 eV, corresponding to the  $\text{Al}_2\text{O}_3$  compound. At the same time, oxygen may be present in nonequivalent chemical states, namely, oxygen entering into aluminum oxide and oxygen entering into other possible phases and structures.



**Figure 5: The Auger Spectra Area of Aluminium at a Depth: a - 0.5 nm; b - 5 nm.**

To identify the chemical state of aluminum, the Auger parameter value was additionally used ( $\alpha = E_{\text{kin}}(\text{Auger}) + E_{\text{sv}}(\text{Al}2p)$ ). The determined values of the Auger parameter are 1461.5 eV and correspond to the aluminum oxidation to 3+

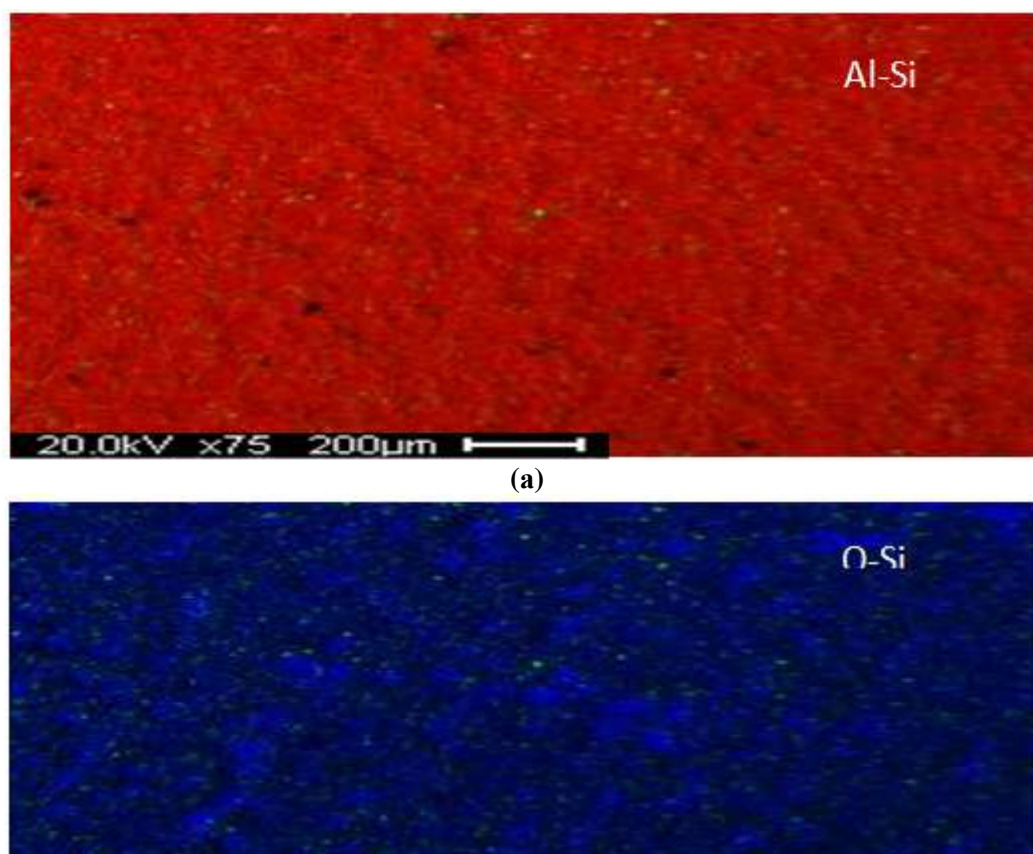
with the formation of  $\text{Al}_2\text{O}_3$ . Table 2 shows the binding energy values of the oxygen and aluminum spectra after the correction of the scale and related to the formation of aluminum oxide.

**Table 2: The Binding Energy Values of the Peaks of O1s, Al2p and Auger Parameter.**

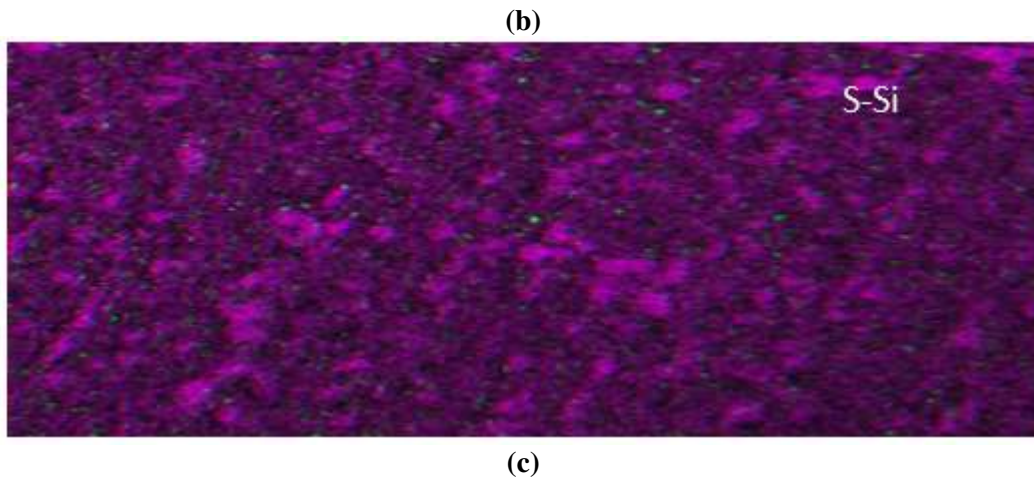
Sample	Depth, nm	O1s	Al2p	Al-Auger	Auger Parameter
575	0	532.2	74.9	100	1461.5
	0.5	531.9	74.9	100	1461.5
	5	531.9	74.9	100	1461.5
564	0	532	74.9	100.2	1461.5
	0.5	531.9	74.9	100.1	1461.5
	5	531.7	74.9	100	1461.5

According to the energy dispersion spectrum from the entire area, in addition to aluminum and oxygen, the samples under study contain sulfur and a slightly increased amount of silicon, which is almost completely located in the substrate in separate areas — the greater the concentration of the element at this point, the higher the brightness of the point. There is a clear correlation between the distribution of aluminum and silicon: where there is silicon, there is no aluminum.

Figure 6 shows the superposition of concentration maps of silicon with aluminum, oxygen and sulfur. From the analysis of concentration maps, it can be seen that silicon (shown in green) is located in areas where these elements are not present. The energy dispersion spectrum was used to calculate the elements concentration of this coating area. Table 3 shows the values corresponding to sample 575.







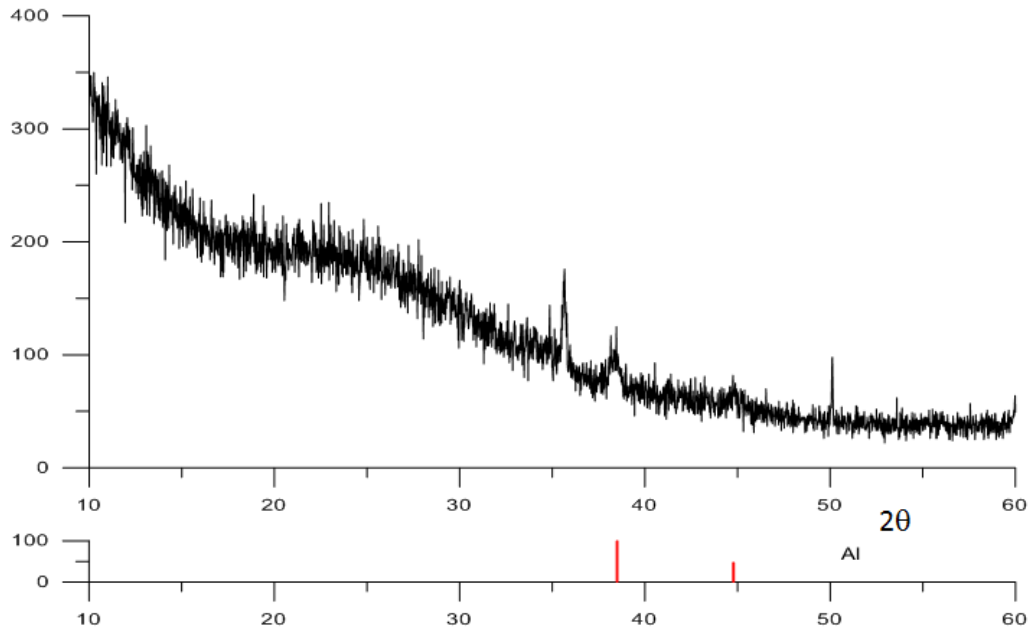
**Figure 6: Superposition of Concentration Maps of Silicon with Aluminum, Oxygen and Sulfur: a- Al-Si;b- O-Si;c- S-Si.**

There is an increased level of oxygen in the formed layer.

**Table 3: The Concentration of Elements in the Surface Layer of Sample 575**

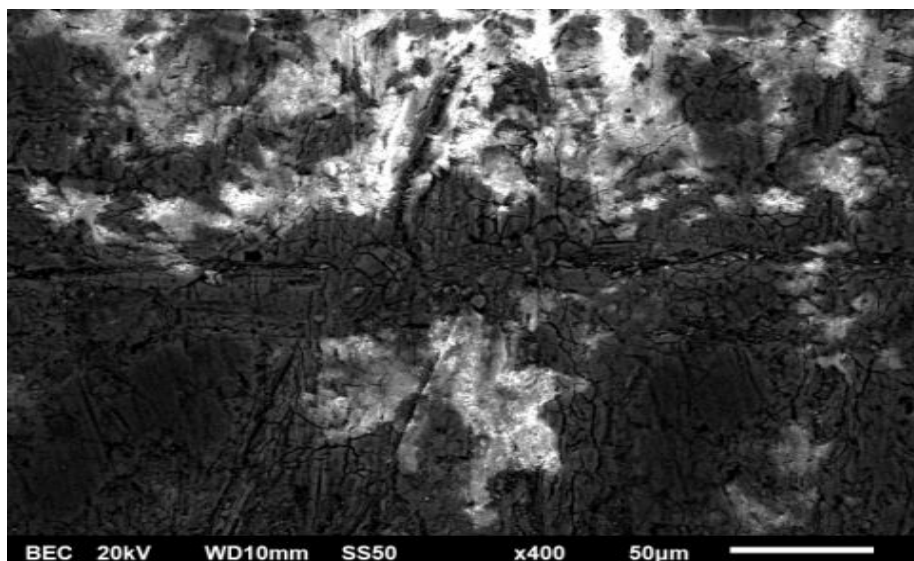
	Al		O		Si		S	
	at.%	wt.%	at.%	wt.%	at.%	wt.%	at.%	wt.%
<b>Coating</b>	31.17	45.07	61.80	45.41	1.92	2.89	2.11	3.63

The phase composition of the samples was studied by x-ray diffraction.



**Figure 7: Diffraction Pattern of Sample 564 in a Sliding Beam.**

Figure 7 shows the diffraction pattern of the surface of sample No. 564 taken in the geometry of the sliding beam. The depth of analysis in this case is comparable to the coating's thickness (peaks from aluminum are not very intense).



**Figure 8: The Surface of the Oxide formed by the Electrode Vibration with a Frequency of 100 Hz.**

The image shows the amorphous component of the structure in the angular range of  $2\Theta$   $20^\circ$ - $30^\circ$ . There is a peak at an angle of  $2\Theta^\circ = 37.77$ , corresponding to  $\gamma$ - $\text{Al}_2\text{O}_3$ . Several peaks at an angle of  $2\Theta^\circ$ : 35.62, 42.10, 59.96 could not be determined due to the lack of an analogue in the program database. Most likely, these are formations of complex compounds.

The oxide layer surface of sample No. 564 at 400-fold magnification is shown in Fig. 8. It can be seen from the figure that the surface is rather porous. The nature of the pores is mostly linear. The phase composition is inhomogeneous, and this can be seen from different color shades.

Table 4 shows the results of the basic parameters of hardening formed on the surface of the alloys during the anode vibration.

**Table 4: The Properties of the Coatings during the Anode Vibration**

Sl. No.	Thickness, $\mu\text{m}$	Hardness, HRC	Frequency, Hz	Bubbling
1	57	65	-	Ozone-airmixture
2	60	68	-	
3	61	69	-	
1	62	71	100	Ozone-airmixture + vibration
2	68	73	200	
3	68	73	300	

## CONCLUSIONS

- Vibration effects change the hydrodynamic conditions in the pore volume as a result of alternating loads in small volumes with pressure changing from maximum to minimum, which causes the destruction of the oxide layer at the initial stage.
- The splitting of gas bubbles of unreacted ozone intensifies the cracks encrustation process and faults, forming a block-textured nature of the coating.
- Anodizing with an oscillating anode improves the mechanical properties of the formed layer by 8–12%.



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## AUTHOR PROFILE



**Nikolai F. Kolenchin**, Doctor of Engineering, Professor, Chief Researcher, Center for Advanced Research and Innovation, Industrial University of Tyumen in Russia.

